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Research Report for

"Theoretical Studies of Nonlinear Optical Properties
of
Conjugated Polymers"

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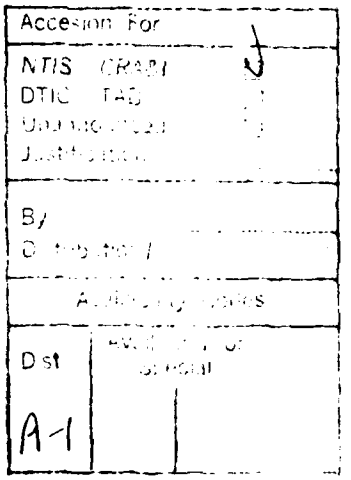

The study of the non-linear optical properties of polymeric systems is a challenging and exciting field of research ranging from device engineering, optical measurements, chemical synthesis to design and theoretical issues. At the present time, most of the basic science needed for the synthesis of molecules and the design of devices utilizing second order optical susceptibilities ($\chi^{(2)}$ or γ) is in hand, although certain issues remain to be resolved. On the other hand, many important questions regarding the design and use of third order optical susceptibilities ($\chi^{(3)}$ or γ) are still unanswered. The earliest ideas of the importance of low dimensionality (and hence the possibility that polymeric materials will be important for the design of devices based on $\chi^{(3)}$) are still qualitatively compelling. In addition, the desire for small (but non-zero) optical band gaps suggests the use of conjugated molecules. At present, there is considerable effort, both experimentally and theoretically, in optimizing the value of γ for polymers or oligomers with conjugated segments, because such conjugated polymers (like polyacetylene, polythiophenes, and the poly-diacetylenes) have very large γ. These polymers have also been under intense scrutiny because of their large conductivities when doped [3]. Although we are beginning to understand the theoretical reasons for the various unusual properties of these materials, we do not understand the factors that limit the ultimate value of γ. For example, what are the important structures and interactions in the molecule that prevent γ from being as large as possible while still having a small absorption coefficient, and how can we design molecules with these constraints in mind. The most important limiting factors for γ in conjugated molecules are electronelectron interactions, vibration-electron interactions, and interchain interactions. I

i) Molecular vibrational effects on γ : Almost all theoretical calculations of the value of γ rely on a straightforward perturbative sum over states method utilizing *electronic* states only. The form of this at zero frequency is:

$$\gamma = \sum \frac{\langle g|\mu|n\rangle\langle n|\mu|m\rangle\langle m|\mu|p\rangle\langle p|\mu|g\rangle}{E_{ng}E_{mg}E_{pg}} - \sum \frac{|\langle g|\mu|n\rangle|^2\,|\langle g|\mu|p\rangle|^2}{E_{ng}E_{pg}} \qquad (1)$$

Here μ is the transition moment operator, E_{ng} is the energy difference between the ground (g) state and the state labelled n, and the sums are restricted so as to exclude the ground state. However, the theory prescribes that the states in the sum should be the eigenstates of the molecular hamiltonian, and thus should contain *vibrational* states as well. One effect of inclusion of the vibrational states, within the Born Oppenheimer approximation, will be the spreading out of the transition strength through

Franck Condon factors with the concomitant change in energy denominators. The effect of spreading the intensities over the vibrational states in the excited electronic state will be to lower the value of γ since the energy denominators for most transitions will become slightly larger, and the numerators will still sum to the same value, because of the Franck Condon sum rules. The presence of a Stokes shift will, on the other hand, increase the value of γ somewhat. But, in most cases the combined effect will be small. Another, and potentially much more important effect will be the inclusion of terms that were previously excluded. Here the intermediate state m can be an excited vibrational state of the *ground* electronic state. These terms will have a very small energy denominator (just a vibrational energy instead of an electronic energy) and thus can be large. If we consider this set of terms alone, and label them $\gamma+$, we find

$$\gamma+ = \sum \frac{|R(0\text{-}> v)|^2}{E_{gv;g0}} \qquad (2)$$

where $R(0\text{-}>v)$ is the Raman amplitude from the lowest vibrational level of the ground electronic state to the v th vibrational level of the ground electronic state:

$$R(0\text{-}> v) = \sum\sum \frac{\langle g0|\mu|p\kappa\rangle\langle p\kappa|\mu|gv\rangle}{E_{p\kappa;g0}}$$

where p represents an excited electronic state and κ represents the κ th vibrational state in that electronic state. We have evaluated the term $\gamma+$ in the Born Oppenheimer approximation using a single vibrational mode, and including both Condon contributions (i.e. terms arising from that part of the electronic transition moment independent of the vibrational coordinate) and Herzberg-Teller terms (i.e. that part of the electronic transition moment depending on vibrational coordinate), but neglecting the effects of Duschinsky rotation

Results are calculated using Huckel theory for simplicity; a calculation based on more adequate electronic structure theories shows the same effect. Note the saturation of the third order polarizability with N, the number of double bonds. We see that the contribution from vibrational states is an order of magnitude smaller than the electronic contribution. Of course, this result is dependent on the assumed Franck-Condon parameters and Herzberg Teller parameters. We have taken values from the polyene literature for our estimate. With these values, the effect of Condon terms is small, and the effect of Herzberg Teller contributions is larger.

Our calculations suggest that, using the values of vibration-electron interaction parameters consistent with short chain polyenes, the effect of vibrations on the third order susceptibility of polyacetylene is small, but

nonnegligible. Other authors have suggested that the vibration-electron interaction parameters in polyacetylene are much larger than we have assumed, leading to a larger effect on γ. This would imply that these interactions change rapidly as the size of the molecule increases. However, there is no experimental evidence for this from the Raman studies of short chain polyenes up to 12 double bonds in conjugation ; nor is there from other theoretical work.

(ii) Simple Anharmonic Oscillator Model for β and γ: As the size of an oligomer increases, the higher order polarizabilities *per unit cell* increase and then saturate even for a perfect polymer with no defects. This saturation occurs at the conjugation length of the polymer. It is of interest to understand the factors that cause the conjugation length to be finite in perfect systems., and in addition, if the conjugation length for different polarizabilities are the same. Huckel theory for polyacetylene predicts that there is one conjugation length determined by the ratio of the band width of the pi electrons to the band gap. It is important to generalize and test this idea on other models. We have used an anharmonic oscillator model to investigate these ideas. Instead of an array of interacting quartic oscillators as a model for the one dimensional polymer, we have used an array of interacting Morse oscillators as a model. This model is more realistic as a model for molecules since the excited states in the Morse potential become closer together as the energy increases, just as in a π electron molecule. Using this model, which is not meant to be quantitative, but rather a qualitative guide to the conjugation length, we find that the conjugation lengths for the various polarizabilities are in fact the same, that the conjugation length decreases as the interaction between units decreases, and is given in this model by the ratio of the band width (due to the interunit interactions) divided by the band gap (here the oscillator frequency)

(iii) Effects of electron electron interactions on γ: Within the independent electron approximation (i.e. Huckel theory or nearly free electron (band) theory applicable to semiconductors), the perturbation theory expression for γ, equation (1), when all the cancellations that occur in this approximation are taken into account , can be written as a sum over two classes of terms. The first class is labelled the electron-hole pair migration term, and comes about when the excited electron in state n (see equation (1)) moves to another orbital in the conduction band to form state m (or when the hole in the valence band is changed to form another hole in the valence band). Using the standard parameters in Huckel theory for polyacetylene, the contributions to γ from these two classes can be calculated and the values for different size molecules (i.e. the number, N, of double bonds) found. We find that the e-h pair migration terms are dominant; the contribution from the doubly excited states results in a 20% decrease of the total value.

:ien electron-electron interactions are included in the Hamiltonian ..ve! of the PPP model (i.e. an extended Hubbard model), the lower excited stat.s of the molecule become tightly bound excitons. These exciton states are most concisely represented by forming the Wannier site functions of the valence and conduction bands (found in the Hartree Fock limit of the PPP model), and forming configurations by taking an electron from one valence-band site function and putting it on a conduction-band site function a distance Δ away. All such configurations (for all Δ)are then used as a basis set for the calculation of the singly excited exciton states. On performing this calculation, we find that a) the oscillator strength from the ground state to the excited states is almost entirely to the lowest exciton state, labelled an s-type exciton (by 20 double bonds, greater than 98% of the total oscillator strength is to this state) and b) the oscillator strength from the first exciton state to higher exciton states (labelled p-type excitons) is similarly saturated. We find that the lowest excited states have an average electron-hole spacing of only ~4-6 double bonds. The neglect of biexciton terms, i.e. those similar to the doubly excited states in the independent electron model is beyond this calculation; however, the argument given above suggests that the contribution of these terms will be small. This has to be carefully checked for small systems, where an exact calculation is possible and the effects of higher order correlations can be estimated. These results suggest that the singly excited excitons should provide enough information for a calculation of the optical properties, including non-linear properties. It is also interesting to see that the free electron theory, or Huckel theory, can be parametrized to fit the exciton calculation reasonably well, suggesting the reasons for the success of the free electron theory.

The results of the above calculation are compared to one in which an exciton calculation is done on a short chain and the subsequent wavefunctions are transferred to a large chain. This "transfer" is done by keeping the form of the exciton function and delocalizing that function over the larger chain. From our calculation, it is clear that the form of the exciton saturates by 10-15 double bonds, and this form can be then transferred to larger chains to reproduce the exact large chain value of γ. Similar results are obtained for α, the linear polarizability.

These calculations suggest that the exciton picture is an efficient and physically reasonable choice for studying polymer non-linear optical properties. It turns out that there are three length scales in this system: the electron-hole separation ($l_{el\text{-}hole}$) for the optically important states saturates at small distances, the length scale at which the form of the excited states saturates (l_{ex}) which is larger than $l_{el\text{-}hole}$, and the length scale at which the optical properties saturate (l_{conj}) due to further delocalization of the exciton wavefunctions on the larger chains. Further refinement of the model and calculations for more complex systems are now possible, as outlined below in the proposal section. Another reassuring result from the independent electron calculation was the rederivation of the Genkin-Mednis formula for γ

using molecular methods rather than methods from semiconductor band theory.

(iv) Non-perturbative Optical Susceptibilities using a Floquet Theory in the Density Matrix Formalism: The Floquet theory is a method for treating the interaction of a molecular system with a time varying electromagnetic field with a few frequency components . In the simplest case of a single frequency field, the molecular states are replaced by combined molecular-field states. The field part of the state is labelled by an integer, n, representing the nth Fourier component. Truncating the problem by neglecting higher Fourier components, we can solve non-perturbatively for the optical susceptibilities. We use the density matrix formalism, so that the effects of relaxation and dephasing can be taken into account for the susceptibility. The results, when expanded in a series in powers of the field reproduces the perturbation theory result, as they should . We have considered a number of molecular model systems, meant to mimic conjugated polymers and have calculated the non-perturbative susceptibility of the system as the ratio of the induced polarization divided by the electric field strength (neglecting directional dependence for ease of presentation):

$$\chi(\omega,E) = P(\omega,E)/E(\omega) \qquad (4)$$

where $P(\omega)$ is calculated by solving for the density matrix of the molecule-field system in the steady state, including relaxation terms and using the transition dipole moments. Note that this form of $\chi(\omega,E)$ is field dependent, and when expanded, reproduces the perturbation result for higher order susceptibilities:

$$\chi(\omega,E)= \chi^{(1)}(\omega) + \chi^{(2)}(\omega)\, E + \chi^{(3)}(\omega)\, E^2 +... \qquad (5)$$

Alternatively, we can define an apparent %(3)(ct),E) (for centro-symmetric systems in which $\chi^{(2)}(\omega) = 0$ by

$$[\chi^{(3)}(\omega,E)]app = [\chi(\omega)-\chi^{(1)}(\omega)] \,/\, E^2 \qquad (6)$$

In this form the higher order terms in the series are taken into account.

Using this formalism, we have performed a number of calculations for a three level system mimicking an oligomer of polyacetylene with 4 double bonds . The first optically accessible excited state (Bu) is at ~37000 cm-1 above the ground state and the higher (nAg) state is at ~58000 cm-1 above the ground state. Note that these are the states connected with the largest transition moments; the well known low lying Ag state has a much smaller transition moment from the Bu state and so can be neglected in first order. We have computed the full $\chi(\omega,E)$, the perturbative $\chi^{(1)}(\omega)$, $[\chi^{(3)}(\omega,E)]app$ and

the perturbative $\chi^{(3)}(\omega)$ for an electric field strength corresponding to 100 MW/cm2. We find that there are large corrections to the optical response of such a system due to higher order terms.

These results show that higher order effects can make a calculable contribution to the non-perturbative optical responses of a conjugated system like polyacetylene, in which the oscillator strengths are largely concentrated in a few states. In addition, we have shown that a simple density matrix model that contains relaxation and dephasing effects on the non-linear optical susceptibilities can be developed and implemented.

Papers published with support of this Grant

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Vibrational Contributions to Third Order Non Linear Susceptibilities, David Yaron and R. Silbey, *J. Chem. Phys.* **95**, 563 (1991)

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